

PAT 99164 PCT
BASF Coatings AG

Highly scratch-resistant multicoat system, its
preparation and use

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5 The present invention relates to a novel, highly
scratch-resistant multicoat clearcoat system based on
at least two coating materials curable with actinic
radiation. The present invention further relates to the
use of the novel, highly scratch-resistant multicoat
clearcoat in automotive OEM finishing and refinish,
10 industrial coating, including coil coating and
container coating, the coating of plastics, and
furniture coating. The present invention further
relates to a novel process for producing multicoat
clearcoat systems.

15 Automobile bodies, plastic parts for automobiles or
domestic appliances, and industrial components are
nowadays protected by a clearcoat. The clearcoat may be
used as the sole coat or else may form the topmost coat
20 of a multicoat topcoat system.

Automobile bodies in particular are provided
extensively with a multicoat topcoat system. Clearcoats
are frequently applied as the final coat. Materials
25 suitable for this purpose are the customary and known
one-component (1K), two-component (2K), multicomponent
(3K, 4K) powder clearcoat or powder slurry clearcoat
materials, or UV-curable clearcoat materials.

One-component (1K), two-component (2K) or
multicomponent (3K, 4K) clearcoat materials are
described, for example, in the patents US-A-5 474 811,
US-A-5 356 669, US-A-5 605 965, WO 94/10 211,
5 WO 94/10 212, WO 94/10 213, EP-A-0 594 068,
EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992,
WO 94/22 969, EP-A-0 596 460 and WO 92/22 615.

10 Powder clearcoat materials are known, for example, from
the German patent DE-A-42 22 194 or from the BASF Lacke
+ Farben AG product information bulletin "Pulverlacke"
[powder coating materials], 1990.

15 A powder coating material which is curable thermally
and with actinic radiation is known from the European
patent EP-A-0 844 286. It comprises an unsaturated
binder and a second resin, copolymerizable with the
first, and also a photoinitiator and a thermal
20 initiator, and is accordingly curable thermally and
with actinic radiation. However, this dual-cure powder
coating material is used as a pigmented topcoat
material, which is cured superficially with UV light
and thermally in the regions close to the substrate.
The patent does not reveal whether this known powder
25 coating material is also suitable for producing
clearcoats, especially in multicoat systems.

Powder slurry coating materials comprise powder coating
materials in the form of aqueous dispersions. Slurries

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of this kind are described, for example, in the U.S. patent US-A-4 268 542 and in the German patent applications DE-A-195 18 392.4 and DE-A-196 13 547 and in the German patent application DE-A-198 14 471.7, which was unpublished at the priority date of the present specification.

UV-curable clearcoat materials are disclosed, for example, by the patents EP-A-0 540 884, EP-A-0 568 967, and US-A-4 675 234.

Each of these clearcoat materials has specific strengths and weaknesses. Using these clearcoat materials, multicoat systems which satisfy the optical requirements are obtained. However, the scratch-resistant one-component (1K) clearcoat materials are sometimes not sufficiently weathering-resistant, whereas the weathering-resistant two-component (2K) or multicomponent (3K, 4K) clearcoat materials are often not sufficiently scratch-resistant. Certain one-component (1K) clearcoat materials are indeed scratch-resistant and weathering-stable but, in combination with frequently employed waterborne basecoat materials, exhibit surface defects such as shrinkage (wrinkling).

Powder clearcoat materials, powder slurry clearcoat materials and UV-curable clearcoat materials, on the other hand, exhibit a not entirely satisfactory

intercoat adhesion, without completely solving the problems of scratch resistance or etch resistance.

EP-A-0 568 967 discloses a process for producing multicoat systems in which a thermally curable clearcoat film is applied by the wet-on-wet technique to a pigmented basecoat film, after which the two films are heat-cured together. Atop the cured clearcoat there is subsequently applied at least one further clearcoat film based on coating materials curable with actinic radiation, and curing is carried out with actinic radiation, or thermally and with actinic radiation. This process gives clearcoats of high chemical resistance and optical quality. However, the scratch resistance is not satisfactory.

Furthermore, EP-A-0 568 967 discloses a process in which a coating material curable with actinic radiation is applied to the pigmented basecoat film and cured. Subsequently, a further coat of the same coating material is applied and is cured with actinic radiation. Although this results in a highly glossy surface without perceptible texture, the clearcoat in question yellows. Additionally, the scratch resistance still leaves something to be desired.

Recently, materials known as sol-gel clearcoats and based on siloxane-containing coating formulations have been developed which are obtained by hydrolysis and condensation of silane compounds. These coating

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materials, which are used as coating compositions on plastics, are described, for example, in the German patents DE-A-43 03 570, 34 07 087, 40 11 045, 40 25 215, 38 28 098, 40 20 316, and 41 22 743.

5 Sol-gel clearcoats impart very good scratch resistance to substrates made of plastic, such as spectacle lenses or motorcycle helmet visors, for example. This scratch resistance is not achieved by the known OEM (original
10 equipment manufacturing) clearcoat materials normally used for the original finishing of vehicles. The automobile industry is now demanding that this improved scratch resistance be transferred to the clearcoats used in the finishing of automobiles as well. The aim
15 here in particular is to provide better protection to those parts of the automobile bodies which are subject to particularly severe stresses, such as hoods, fenders, sills or doors in the door-handle region.

20 Replacing the OEM clearcoat materials or OEM powder slurry clearcoat materials commonly used in automotive finishing by sol-gel clearcoat materials, however, is not immediately possible, since the clearcoats are too brittle for this purpose, for example, or because the
25 optical properties (appearance) achieved during the attempt to adapt them to the OEM requirements are in many cases poor. Furthermore, they cannot be applied at thicknesses above 8 to 10 μm . Moreover, constituents of the sol-gel clearcoat materials may "strike through"

during their drying and/or curing: that is, they are absorbed by the substrate, and, as a result, the clearcoats in question lose hardness. Above all, however, the sol-gel clearcoat materials are too
5 expensive.

The economically more favorable use of the sol-gel clearcoat materials as an additional coat over the clearcoats used to date gives rise to adhesion problems
10 within the multicoat clearcoat system, between the clearcoat and the sol-gel coat, these problems arising in particular after stone chipping and on exposure to condensation. In some cases this problem is exacerbated by the adhesion between the clearcoat and the substrate
15 also being affected.

These problems may be solved to a certain extent by subjecting the clearcoat film that is to be coated with the sol-gel clearcoat material to only partial curing,
20 so that on conjoint curing the sol-gel coating may be anchored chemically, so to speak, on the clearcoat film. However, the second clearcoat film requires a long oven drying time to cure, which is a considerable disadvantage.

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It is an object of the present invention to provide a novel multicoat clearcoat system which no longer has the disadvantages of the prior art but which instead is easy to produce, highly scratch-resistant, stable to

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weathering, free from yellowing, hard, flexible, and free from surface defects, exhibits a high level of adhesion to all substrates and within the clearcoat system too, and may be produced in the high coat
5 thickness needed for an outstanding overall appearance. A further object of the present invention is to provide a new process for producing such single-coat or multicoat clearcoats from at least two coating materials curable with actinic radiation.

10

Accordingly we have found the novel, highly scratch-resistant multicoat clearcoat system A for a primed or unprimed substrate, said system being producible by

15 (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, and partially curing it, and

20 (2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

25

(3) curing the clearcoat films I and II conjointly with actinic radiation and thermally.

As an alternative to this, we have found the further novel, highly scratch-resistant multicoat clearcoat system A for a primed or unprimed substrate, said system being producible by

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- (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, curing it and roughening it,

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- (2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then

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- (3) curing the clearcoat film II with actinic radiation and, if desired, thermally.

20 The two novel, highly scratch-resistant multicoat clearcoat systems A are referred to below as the "clearcoat systems A of the invention".

We have also found the novel process for producing a
25 highly scratch-resistant multicoat clearcoat system A on a primed or unprimed substrate, which involves

- (1) applying at least one clearcoat film I of a coating material I curable thermally and with

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actinic radiation to the surface of the substrate,
and partially curing it, and

- 5 (2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then
- 10 (3) curing the clearcoat film I and II conjointly with actinic radiation and thermally.

As an alternative to this, we have found the further novel process for producing a highly scratch-resistant multicoat clearcoat system A on a primed or unprimed substrate, which involves

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- (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, curing it and roughening it,
- 20

- (2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then
- 25

- (3) curing the clearcoat film II with actinic radiation and, if desired, thermally.

The two new processes for producing highly scratch-resistant clearcoat systems A are referred to below as "processes A of the invention".

We have additionally found the novel, highly scratch-resistant multicoat color and/or effect coating system B for a primed or unprimed substrate, which is producible by

- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,
- (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them, and
- (3) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

(4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.

5 As an alternative to this, we have also found the novel, highly scratch-resistant multicoat color and/or effect coating system B for a primed or unprimed substrate, which is producible by

10 (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,

15 (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,

20 (3) curing the basecoat film III and clearcoat film(s) I conjointly, thermally and with actinic radiation,

25 (4) roughening the outer surface of the clearcoat film(s) I,

(5) applying a further clearcoat film II of a coating material II curable with actinic radiation and

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also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then

- 5 (6) curing the clearcoat film II with actinic radiation and, if desired, thermally.

In the text below, the novel multicoat color and/or effect coating systems B are referred to as the
10 "multicoat systems B of the invention".

Furthermore, we have found the novel process for producing a highly scratch-resistant multicoat color and/or effect coating system B of a primed or unprimed
15 substrate, which involves

- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with
20 actinic radiation to the surface of the substrate and drying it without curing,
- (2) applying at least one clearcoat film I of a coating material I curable thermally and with
25 actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them, and
- (3) applying a further clearcoat film II of a coating material II curable with actinic radiation and

also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

- 5 (4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.

As an alternative to this, we have found the further
10 novel process for producing a highly scratch-resistant multicoat color and/or effect coating system B on a primed or unprimed substrate, which involves

- 15 (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,
- 20 (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,
- 25 (3) curing the basecoat film III and clearcoat film(s) I conjointly, thermally and with actinic radiation,

(4) roughening the outer surface of the clearcoat film(s) I,

5 (5) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then

10 (6) curing the clearcoat film II with actinic radiation and also, if desired, thermally.

In the text below, the two new processes are referred to as the "processes B of the invention".

15

In the context of the present invention, the term "thermal curing" denotes the heat-initiated curing of a film of a coating material, usually using a separate crosslinking agent. This is commonly referred to by those in the art as external crosslinking. Where the crosslinking agents have already been built into the binders, the term self-crosslinking is used. In accordance with the invention, external crosslinking is of advantage and is therefore employed with preference.

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In the context of the present invention, actinic radiation means electron beams or, preferably, UV radiation. Curing by UV radiation is normally initiated by free-radical or cationic photoinitiators and in

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terms of its mechanism is a free-radical or cationic photopolymerization.

Where thermal curing and curing with actinic light are employed conjointly for one coating material, the term "dual cure" is also used.

In the light of the prior art it was surprising and unforeseeable for the skilled worker that the very complex problem on which the present invention is based might be solved with the aid of the clearcoat system A of the invention and of the multicoat system B of the invention and also of the processes of the invention for producing them. A particular surprise is that not only the intercoat adhesion within the clearcoat system A of the invention but also the adhesion to the basecoat III within the multicoat system B of the invention are improved to an extent far beyond that known. The clearcoat system A of the invention and the multicoat system B of the invention have excellent optical properties, in particular a high level of fullness, high DOI values, high gloss, and no yellowing. As a consequence of the dual curing, even complex components and shaped parts may be fully cured in their shadow regions in a simple manner. With all these advantages, the clearcoat system A of the invention and the multicoat system B of the invention are also of outstanding weathering and chemical stability. Not least, however, they are extremely

scratch-resistant and withstand even treatment with steel wool. In particular, however, they are not damaged by the equipment commonly employed in carwash installations.

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The clearcoat system A of the invention is outstandingly suitable for the coating of a primed or unprimed substrate.

- 10 Suitable coating substrates are all surfaces which are amenable to combined curing using heat and actinic radiation, examples being metals, plastics, wood, ceramic, stone, textile, fiber composites, leather, glass, glass fibers, glass wool, rockwool, mineral- and
- 15 resin-bound building materials, such as plasterboard, cement slabs or rooftiles. Accordingly, the clearcoat system A of the invention is also suitable for applications outside of automotive finishing, in particular for the coating of furniture and for
- 20 industrial coating, including coil coating and container coating. In the context of industrial coatings, it is suitable for coating virtually all parts for private or industrial use, such as radiators, domestic appliances, small metal parts, hub caps or
- 25 wheel rims. The clearcoat system A of the invention is particularly suitable as a coating for basecoats, preferably in the automobile industry. It is particularly suitable as a clearcoat over waterborne basecoats based on polyesters, polyurethane resins and

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amino resins, especially as part of the multicoat system B of the invention.

With the clearcoat system A of the invention or with
5 the multicoat system B of the invention it is also
possible, in particular, to coat primed or unprimed
plastics such as, for example, ABS, AMMA, ASA, CA, CAB,
EP, UF, CF, MF, MPF, PF, PAN, PA, PE, HDPE, LDPE,
LLDPE, UHMWPE, PET, PMMA, PP, PS, SB, PUR, PVC, RF,
10 SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM and UP
(abbreviations to DIN 7728T1). The plastics to be
coated may of course also comprise polymer blends,
modified plastics, or fiber-reinforced plastics. The
system may also be used to coat plastics commonly used
15 in vehicle construction, especially motor vehicle
construction.

Nonfunctionalized and/or nonpolar substrate surfaces
may be subjected prior to coating in a known manner to
20 a pretreatment, such as with a plasma or by flaming.

The clearcoat system A of the invention is producible
by, in a first process step, applying at least one
clearcoat film I of a coating material I curable
25 thermally and with actinic radiation to the surface of
the substrate.

Accordingly, in the context of the present invention,
it is possible to apply only one clearcoat film I of

the coating material I. However, two or more such clearcoat films I may be applied. In this case, different coating materials I may be employed to construct the clearcoat films I. In the majority of cases, however, the target properties profile of the clearcoat system A of the invention is achieved with one clearcoat film I.

The clearcoat film I is applied in a wet film thickness such that curing results, in the finished clearcoat system A of the invention, in a dry film thickness of from 10 to 100, preferably from 15 to 75, with particular preference from 20 to 55, and in particular from 20 to 35 μm .

The application of the coating material I for the purpose of producing the clearcoat film I may take place by any customary application method, such as spraying, knife coating, brushing, flow coating, dipping or rolling, for example. Preference is given to using spray application methods, such as compressed air spraying, airless spraying, high-speed rotation, electrostatic spray application (ESTA), alone or in conjunction with hot spray application such as hot-air spraying, for example. The applications may be implemented at temperatures of max. 70 to 80° Celsius, so that appropriate application viscosities are achieved without any change or damage to the coating material I, or its overspray, which may be intended for

reprocessing, during the short period of thermal stress. For instance, hot spraying may be configured such that the coating material I is heated only very shortly in, or shortly before, the spray nozzle.

5

The spray booth used for the application may be operated, for example, with an optionally thermostatable recirculation system which is operated with an appropriate absorption medium for the
10 overspray, an example of such a medium being the coating material I itself.

Application is preferably conducted under illumination with visible light with a wavelength of more than
15 550 nm, or with light excluded. This prevents material change or damage to the coating material I or the overspray.

Of course, the above-described application methods may
20 also be employed for the production of the clearcoat film II or the basecoat film III and also, if desired, further coating films, in the context of the processes A or B of the invention.

25 In accordance with the invention, the clearcoat film I is partially cured following its application. Viewed in terms of its methodology, the partial curing does not differ from the customary full curing of a coating film. In this case, crosslinking is carried out only

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until the clearcoat film I possesses, on the one hand,
a dimensional stability sufficient for the purposes of
the processes A or B of the invention and, on the other
hand, a sufficient amount of the crosslinkable
5 functional groups (a11) and (a21) and/or (a12) and
(a22) (complementary functional groups) described below
for subsequent crosslinking and for intercoat adhesion.
The extent of partial curing may therefore vary very
widely and is guided by the requirements of each
10 individual case. However, it may be determined by the
skilled worker on the basis of his or her general
knowledge in the art and/or on the basis of simple
preliminary tests. Of the crosslinkable functional
groups present in the coating material I, preferably
15 from 0.5 to 99.5, with particular preference from 1 to
99, with very particular preference from 2 to 90, and
in particular from 3 to 80 mol% are reacted. It is
especially preferable if the clearcoat film I is still
tacky following its partial curing.

20

In accordance with the invention, clearcoat film I may
be partially cured with actinic radiation or thermally,
or with actinic radiation and thermally. In accordance
with the invention it is of advantage to cure the
25 clearcoat film I partially with actinic radiation,
since in this case it is possible to exert particularly
effective control over the degree of crosslinking by
way of the input of radiative energy.

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Curing may take place after a certain rest period. This period may last for from 30 seconds to 2 hours, preferably for from 1 minute to 1 hour, and in particular for from 1 minute to 30 minutes. The rest
5 period is used, for example, for leveling and for devolatilization of the clearcoat I or for the evaporation of volatile constituents such as solvents, water, or carbon dioxide if the coating material has been applied using supercritical carbon dioxide as
10 solvent. The rest period may be assisted and/or shortened by the application of elevated temperatures up to 80° Celsius, provided this does not entail any damage or change to the clearcoat film I, such as premature complete crosslinking, for instance.

15 In accordance with the invention, curing with actinic radiation takes place with UV radiation or electron beams. If desired, it may be carried out, or supplemented, with actinic radiation from other
20 sources. In the case of electron beams, it is preferred to operate under an inert gas atmosphere. This may be ensured, for example, by supplying carbon dioxide and/or nitrogen directly to the surface of the clearcoat film I.

25 In the case of curing with UV radiation as well it is possible to operate under inert gas in order to prevent the formation of ozone.

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Curing with actinic radiation is carried out using the customary and known radiation sources and optical auxiliary measures. Examples of suitable radiation sources are high- or low-pressure mercury vapor lamps, with or without lead doping in order to open up a radiation window up to 405 nm, or electron beam sources. The arrangement of these emitters is known in principle and may be adapted to the circumstances of the workpiece and the process parameters. In the case of workpieces of complex shape such as automobile bodies, those regions not accessible to direct radiation (shadow regions) such as cavities, folds and other structural undercuts may be (partially) cured using pointwise, small-area or all-round emitters in conjunction with an automatic movement means for the irradiation of cavities or edges.

The equipment and conditions for these curing methods are described, for example, in R. Holmes, U.V. and E.B. Curing Formulations for Printing Inks, Coatings and Paints, SITA Technology, Academic Press, London, United Kingdom 1984.

The (partial) curing here may take place in stages, i.e., by multiple exposure to light or to actinic radiation. It may also take place alternately, i.e., by curing alternately with UV radiation and electron beams.

Thermal curing as well has no special features in terms of its method but instead takes place in accordance with the customary and known methods, such as heating in a forced air oven or irradiation with IR lamps. As
5 with actinic radiation curing, thermal curing may also take place in stages. Thermal curing takes place advantageously at a temperature of from 50 to 100°C, with particular preference from 80 to 100°C, and in particular from 90 to 100°C for a period of from 1 min
10 up to 2 h, with particular preference from 2 min up to 1 h, and in particular from 3 min to 30 min. Where the substrates used have a high capacity to withstand thermal stress, thermal crosslinking may be conducted even at temperatures above 100°C. In this case it is
15 generally advisable for the temperatures used not to exceed 180°C, preferably 160°C, and in particular 140°C.

Where thermal curing and actinic radiation curing are
20 employed together, these methods may be used simultaneously or in alternation. Where the two curing methods are used in alternation, it is possible, for example, to commence with thermal curing and to end with actinic radiation curing. In other cases it may
25 prove advantageous to begin and to end with actinic radiation curing. The skilled worker is able to determine the curing method most advantageous for the case in hand on the basis of his or her general

knowledge in the art, possibly with the assistance of simple preliminary tests.

Of course, the curing methods described above may also be employed for the production of the clearcoat film II or the basecoat film III and also, if desired, further coating films in the context of the processes A or B of the invention.

10 The coating material I for use in accordance with the invention for the production of the clearcoat film I comprises at least one constituent (a1) containing at least two functional groups (a11) which serve for crosslinking with actinic radiation.

15 Examples of suitable functional groups (a11) are epoxide groups or olefinically unsaturated double bonds, as present in vinyl, allyl, cinnamoyl, methacryloyl or acryloyl groups, especially
20 methacryloyl or acryloyl groups. As is known, the epoxide groups are used for cationic photopolymerization, whereas the olefinically unsaturated double bonds are primarily suitable for free-radical photopolymerization. In accordance with
25 the invention, the constituent (a1) may contain epoxide groups and olefinic double bonds, so that it may be subjected to crosslinking with actinic radiation by both mechanisms. It is of advantage, however, to use

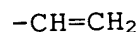
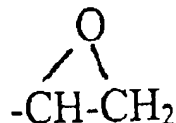
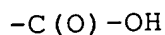
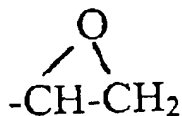
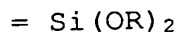
exclusively olefinically unsaturated double bonds of the abovementioned kind as functional groups (a11).

The constituent (a1) for use in accordance with the invention may further comprise at least one, preferably at least two functional group(s) (a12) which are able to undergo thermal crosslinking reactions with the complementary functional groups (a22) of the constituent (a2) described below.

Examples of suitable complementary functional groups (a12) and (a22) are evident from the overview below, in which R represents organic groups.

Overview: Examples of complementary functional groups (a12) and (a22) in the

<u>Constituent (a1) and Constituent (a2)</u>	
or	
<u>Constituent (a2) and Constituent (a1)</u>	
-SH	-C(O)-OH
-NH ₂	-C(O)-O-C(O)-
-OH	-NCO
	-NH-C(O)-OR
	-CH ₂ -OH
	-CH ₂ -O-CH ₃
	-NH-C(O)-CH(-C(O)OR) ₂
	-NH-C(O)-CH(-C(O)OR)(-C(O)-R)



The selection of the respective complementary groups (a12) and (a22) is guided firstly by the consideration that they should not undergo any unwanted reactions initiated by actinic radiation or should not disrupt or inhibit the curing with actinic radiation, and secondly by the temperature range within which thermal curing is to take place. In this context it is of advantage in accordance with the invention, especially with regard to heat-sensitive substrates such as plastics, to choose a temperature range which does not go beyond 100°C, especially 80°C. In the light of these boundary conditions, hydroxyl groups and isocyanate groups have proven advantageous as complementary functional groups, and so are employed with preference in accordance with

the invention. Particular advantages result if the hydroxyl groups are used as functional groups (a12) and the isocyanate groups as functional groups (a22).

5 Where there is no functional group (a12) in the constituent (a1), the coating material I mandatorily includes at least one thermally curable constituent (a7), which is described in detail below.

10 Accordingly, the particularly advantageous constituent (a1) comprises an oligomeric or polymeric compound curable with actinic radiation or thermally which comprises, if desired, at least one, preferably at least two, and in particular at least three hydroxyl
15 group(s) (a12) and at least two and especially three (meth)acryloyl groups (a11).

In the context of the present invention, an oligomeric compound is a compound containing in general on average
20 from 2 to 15 repeating basic structures or monomer units. A polymeric compound, in contrast, is a compound containing in general on average at least 10 repeating basic structures or monomer units. Compounds of this kind are also referred to by those in the art as
25 binders or resins.

In contradistinction thereto, a low molecular mass compound in the context of the present invention is a compound which derives substantially only from one

basic structure or one monomer unit. Compounds of this kind are generally referred to by those in the art as reactive diluents.

- 5 The polymers or oligomers used as binders (a1) normally have a number-average molecular weight of from 500 to 50 000, preferably from 1 000 to 5 000. They preferably have a double bond equivalent weight of from 400 to 2 000, with particular preference from 500 to 900.
- 10 Moreover, at 23°C, they preferably have a viscosity of from 250 to 11 000 mPas. They are employed preferably in an amount of from 5 to 90% by weight, with particular preference from 10 to 80% by weight, and in particular from 15 to 70% by weight, based in each case
- 15 on the overall amount of the coating material I.

Examples of suitable binders or resins (a1) come from the oligomer and/or polymer classes of the (meth)acryloyl-functional (meth)acrylic copolymers, polyether acrylates, polyester acrylates, polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates and phosphazene acrylates and the corresponding methacrylates. It is preferred to use binders (a1) which are free from aromatic structural units. Preference is therefore given to the use of urethane (meth)acrylates, phosphazene (meth)acrylates and/or polyester (meth)-acrylates, with particular preference urethane

(meth)acrylates, especially aliphatic urethane
(meth)acrylates.

5 The urethane (meth)acrylates (a1) are obtained by
reacting a diisocyanate or polyisocyanate with a chain
extender from the group of the diols/polyols and/or
diamines/polyamines and/or dithiols/polythiols and/or
alkanolamines and subsequently reacting the remaining
10 free isocyanate groups with at least one hydroxyalkyl
(meth)acrylate or hydroxyalkyl ester of other
ethylenically unsaturated carboxylic acids.

20 The amounts of chain extender, diisocyanate and/or
polyisocyanate and hydroxyalkyl ester are in this case
preferably chosen so that

- 1.) the ratio of equivalents of the NCO groups to the
reactive groups of the chain extender (hydroxyl,
amino and/or mercaptyl groups) is between 3:1 and
20 1:2, preferably 2:1 and
- 2.) the OH groups of the hydroxyalkyl esters of the
ethylenically unsaturated carboxylic acids are
present in stoichiometric amount in relation to
25 the remaining free isocyanate groups of the
prepolymer formed from isocyanate and chain
extender.

It is also possible to prepare the urethane (meth)acrylates (a1) by first reacting some of the isocyanate groups with a diisocyanate or polyisocyanate with at least one hydroxyalkyl ester and then reacting the remaining isocyanate groups with a chain extender. In this case as well the amounts of chain extender, isocyanate and hydroxyalkyl ester are chosen so that the ratio of equivalents of the NCO groups to the reactive groups of the chain extender is between 3:1 and 1:2, preferably 2:1, and the ratio of equivalents of the remaining NCO groups to the OH groups of the hydroxyalkyl ester is 1:1. Of course, all intermediate forms between these two processes are also possible. For example, some of the isocyanate groups of a diisocyanate may first be reacted with a diol, after which a further portion of the isocyanate groups may be reacted with the hydroxyalkyl ester, and, subsequently, the remaining isocyanate groups may be reacted with a diamine.

20

These various preparation processes of the urethane (meth)acrylates (a1) are known (cf., e.g., EP-A-204 161).

25 Flexibilization of the urethane (meth)acrylates (a1) is possible, for example, by reacting corresponding isocyanate-functional prepolymers or oligomers with relatively long-chain aliphatic diols and/or diamines, especially aliphatic diols and/or diamines having at

least 6 carbon atoms. This flexibilization reaction may be carried out before or after the addition of acrylic or methacrylic acid onto the oligomers or prepolymers.

5 Examples of suitable urethane (meth)acrylates (a1) that may be mentioned include the following, commercially available, polyfunctional aliphatic urethane acrylates:

- 10 - Crodamer® UVU 300 from Croda Resins Ltd, Kent, United Kingdom;
- Genomer® 4302, 4235, 4297 or 4316 from Rahn Chemie, Switzerland;
- Ebecryl® 284, 294, IRR351, 5129 or 1290 from UCB, Drogenbos, Belgium;
- 15 - Roskydal® LS 2989 or LS 2545 or V94-504 from Bayer AG, Germany;
- Viaktin® VTE 6160 from Vianova, Austria; and
- Laromer® 8861 from BASF AG, and experimental products derived therefrom by modification.

20

An example of a suitable phosphazene (meth)acrylate (a1) is the phosphazene dimethacrylate from Idemitsu, Japan.

25 The coating material I of the invention further comprises a constituent (a2).

This constituent (a2) also comprises a resin as defined above for the description of the resins (a1).

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Accordingly, the resins (a2) also come from the oligomer and polymer classes described above. Of advantage in this context are the (meth)acryloyl-functional (meth)acrylic copolymers, which are
5 therefore used with preference in accordance with the invention as resins (a2).

The resins (a2) are employed in an amount of preferably from 5 to 90% by weight, with particular preference
10 from 10 to 80% by weight, and in particular from 15 to 70% by weight, based in each case on the overall amount of the coating material I.

The resins (a2) contain at least two, in particular at
15 least three functional groups (a21) which serve for crosslinking with actinic radiation. Examples of suitable functional groups (a21) for use in accordance with the invention are the functional groups (a11) described above.

20 The resins (a2) further comprise at least one, preferably at least two and in particular at least three functional group(s) (a22) which serve for thermal crosslinking. Examples of suitable such functional
25 groups may be taken from the above overview. Isocyanate groups are particularly advantageous in this context and are therefore used with very particular preference in accordance with the invention as functional groups (a22). Particular advantages result if the resins (a2)

have an isocyanate group (a22) content of from 7 to 20% by weight, with particular preference from 8 to 18% by weight, and in particular from 9 to 17% by weight, based in each case on the resin (a2).

5

Examples of suitable resins (a2) of the type described above are described, for example, in the patents US-A-5 234 970, EP-A-0 549 116, and EP-A-0 618 244.

10 The coating material I for use in accordance with the invention may comprise at least one photoinitiator (a3). If the coating material I or the clearcoat film I is to be crosslinked with UV radiation, the use of a photoinitiator (a3) is generally necessary. Where they
15 are used, they are present in the coating material I preferably in fractions of from 0.1 to 10% by weight, from 1 to 8% by weight, and in particular from 2 to 6% by weight, based in each case on the overall amount of the coating material I.

20

Examples of suitable photoinitiators are those of the Norrish II type, whose mechanism of action is based on an intramolecular variant of the hydrogen abstraction reactions which occur diversely in photochemical
25 reactions (reference may be made here, by way of example, to Römpp Chemie Lexikon, 9th, expanded and revised edition, Georg Thieme Verlag, Stuttgart, Vol. 4, 1991) or cationic photoinitiators (reference may be made here, by way of example, to Römpp Lexikon Lacke

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und Druckfarben, Georg Thieme Verlag, Stuttgart, 1998, pages 444 to 446), especially benzophenones, benzoin or benzoin ethers, or phosphine oxides. It is also possible, for example, to use the products available commercially under the names Irgacure® 184, Irgacure® 1800 and Irgacure® 500 from Ciba Geigy, Grenocure® MBF from Rahn, and Lucirin® TPO from BASF AG.

In addition to the photoinitiators (a3), it is possible to use customary sensitizers such as anthracene in effective amounts.

Furthermore, the coating material I may comprise at least one thermal crosslinking initiator (a4). At from 80 to 120°C, these initiators form free radicals which start the crosslinking reaction. Examples of thermally labile free-radical initiators are organic peroxides, organic azo compounds or C-C-cleaving initiators such as dialkyl peroxides, peroxocarboxylic acids, peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azo dinitriles, or benzpinacol silyl ethers. Particular preference is given to C-C-cleaving initiators, since their thermal cleavage does not produce any gaseous decomposition products which might lead to defects in the coating film. Where used, their amounts are generally from 0.1 to 10, preferably from 0.5 to 8, and in particular from 1 to 5% by weight, based in each case on the overall amount of the coating material I.

Moreover, the coating material I may comprise at least one reactive diluent (a5) curable thermally and/or with actinic radiation.

- 5 Examples of suitable thermally crosslinkable reactive diluents (a5) are oligomeric polyols obtainable from oligomeric intermediates themselves obtained by metathesis reactions from acyclic monoolefins and cyclic monoolefins, by hydroformylation and subsequent
- 10 hydrogenation.

Examples of suitable cyclic monoolefins are cyclobutene, cyclopentene, cyclohexene, cyclooctene, cycloheptene, norbornene or 7-oxanorbornene.

- 15 Examples of suitable acyclic monoolefins are present in hydrocarbon mixtures obtained in petroleum processing by cracking (C₅ cut).

- 20 Examples of suitable oligomeric polyols (a5) for use in accordance with the invention have a hydroxyl number (OHN) of from 200 to 450, a number-average molecular weight Mn of from 400 to 1 000, and a mass-average molecular weight Mw of from 600 to 1 100.

- 25 Further examples of suitable thermally crosslinkable reactive diluents (a5) are hyperbranched compounds containing a tetrafunctional central group, derived from ditrimethylolpropane, diglycerol, ditrimethylol-

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ethane, pentaerythritol, tetrakis(2-hydroxyethyl)-methane, tetrakis(3-hydroxypropyl)methane or 2,2-bishydroxymethyl-1,4-butanediol (homopentaerythritol).

These reactive diluents may be prepared in accordance with the customary and known methods of preparing hyperbranched and dendrimeric compounds. Suitable synthesis methods are described, for example, in the patents WO 93/17 060 and WO 96/12 754 or in the book by G.R. Newkome, C.N. Moorefield and F. Vögtle, "Dendritic Molecules, Concepts, Syntheses, Perspectives", VCH, Weinheim, New York, 1996.

Further examples of suitable reactive diluents (a5) are polycarbonatediols, polyesterpolyols, poly(meth)-acrylatediols, and hydroxyl-containing polyadducts.

Examples of suitable reactive solvents which may be used as reactive diluents (a5) are butyl glycol, 2-methoxypropanol, n-butanol, methoxybutanol, n-propanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, trimethylolpropane, ethyl 2-hydroxypropionate and 3-methyl-3-methoxybutanol, and also derivatives based on propylene glycol, e.g., ethoxyethyl propionate, isopropoxypropanol or methoxypropyl acetate.

Examples of reactive diluents (a5) used that may be crosslinked with actinic radiation are (meth)acrylic acid and esters thereof, maleic acid and its esters, including monoesters, vinyl acetate, vinyl ethers, vinylureas, and the like. Examples that may be mentioned include alkylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, vinyl (meth)acrylate, allyl (meth)acrylate, glycerol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylol-propane di(meth)acrylate, styrene, vinyltoluene, divinylbenzene, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipropylene glycol di(meth)acrylate, hexanediol di(meth)acrylate, ethoxyethoxyethyl acrylate, N-vinylpyrrolidone, phenoxyethyl acrylate, dimethylaminoethyl acrylate, hydroxyethyl (meth)acrylate, butoxyethyl acrylate, isobornyl (meth)acrylate, dimethylacrylamide, and dicyclopentyl acrylate, and also the long-chain linear diacrylates described in EP-A-0 250 631 and having a molecular weight of from 400 to 4 000, preferably from 600 to 2 500. The two acrylate groups may, for example, be separated by a polyoxybutylene structure. Further candidates for use are 1,12-dodecyl diacrylate and the reaction product of 2 mol of acrylic acid with one mole of a dimeric fatty alcohol having generally 36 carbon atoms. Mixtures of the abovementioned monomers are also suitable.

Preferred for use as reactive diluents (a5) are mono- and/or diacrylates, such as isobornyl acrylate, hexanediol diacrylate, tripropylene glycol diacrylate, Laromer® 8887 from BASF AG, and Actilane® 423 from Akcros Chemicals Ltd., UK, for example. Particular preference is given to the use of isobornyl acrylate, hexanediol diacrylate, and tripropylene glycol diacrylate.

10 Where used, the reactive diluents (a5) are employed in an amount of preferably from 2 to 70, with particular preference from 10 to 65, and in particular from 15 to 50% by weight, based in each case on the overall amount of the coating material I.

15 The coating material may further comprise one or more customary coatings additives (a6) in effective amounts, i.e., in amounts of preferably up to 20% by weight, with particular preference up to 15% by weight, and in particular up to 10% by weight, based in each case on the overall amount of the coating material I.

Examples of suitable coatings additives (a6) are

25 - UV absorbers;

- light stabilizers such as HALS compounds, benzotriazoles or oxalanilides;

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- free-radical scavengers;
- crosslinking catalysts such as dibutyltin dilaurate or lithium decanoate;
- slip additives;
- 5 - polymerization inhibitors;
- defoamers;
- emulsifiers, especially nonionic emulsifiers such as alkoxyated alkanols and polyols, phenols and alkylphenols or anionic emulsifiers such as alkali metal salts or ammonium salts of alkanecarboxylic acids, 10 alkanesulfonic acids, and sulfo acids of alkoxyated alkanols and polyols, phenols and alkylphenols;
- wetting agents such as siloxanes, fluorine compounds, carboxylic monoesters, phosphoric esters, polyacrylic acids and their copolymers, or polyurethanes; 15
- adhesion promoters such as tricyclodecanedimethanol;
- leveling agents;
- film-forming auxiliaries such as cellulose derivatives;
- transparent pigments such as silica;
- 20 - flame retardants; or

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- flattening agents.

Further examples of suitable coatings additives (a6) are described in the textbook "Lackadditive" [Additives for coatings] by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998.

Not least, the coating material I may comprise at least one thermally curable constituent (a7) in minor amounts. In the context of the present invention, "minor amounts" are amounts which do not adversely affect the dual-cure properties of the coating material I but instead vary them advantageously. Where used, their proportion in the coating material I should not exceed generally 40% by weight, preferably 35% by weight, and especially 30% by weight.

Examples of suitable constituents (a7) are the binders and crosslinking agents known from the thermally curable coating materials.

Examples of suitable binders (a7) are linear and/or branched and/or block, comb and/or random poly(meth)acrylates or acrylate copolymers, polyesters, alkyds, amino resins, polyurethanes, polylactones, polycarbonates, polyethers, epoxyresin-amine adducts, (meth)acrylatediols, partially saponified polyvinyl esters or polyureas, of which the acrylate copolymers,

the polyesters, the polyurethanes, the polyethers, and the epoxyresin-amine adducts are advantageous.

Suitable binders (a7) are sold, for example, under the trade names Desmophen® 650, 2089, 1100, 670, 1200 and 2017 by Bayer, under the trade names Priplas and Pripol® by Uniqema, under the trade names Chempol® polyester or polyacrylate-polyol by CCP, under the trade names Crodapol® 0-85 and 0-86 by Croda, or under the trade name Formrez® ER417 by Witco.

Examples of suitable crosslinking agents (a7) are blocked diisocyanates and/or polyisocyanates.

Examples of suitable diisocyanates and/or polyisocyanates for preparing the block derivatives (a7) are organic polyisocyanates, especially so-called paint polyisocyanates, having free isocyanate groups attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic moieties. Preference is given to polyisocyanates having from 2 to 5 isocyanate groups per molecule and viscosities of from 100 to 10 000, preferably from 100 to 5 000, and in particular from 100 to 2 000 mPas (at 23°C). If desired, small amounts of organic solvent, preferably from 1 to 25% by weight based on straight polyisocyanate, may be added to the polyisocyanates in order to make it easier to incorporate the isocyanate and, if appropriate, to reduce the viscosity of the polyisocyanate to a level

within the abovementioned ranges. Examples of suitable solvent additives to the polyisocyanates are ethoxyethyl propionate, amyl methyl ketone, and butyl acetate. Furthermore, the polyisocyanates may have been hydrophilically or hydrophobically modified in a customary and known manner.

Examples of suitable polyisocyanates are described, for example, in "Methoden der organischen Chemie", Houben-Weyl, Volume 14/2, 4th Edition, Georg Thieme Verlag, Stuttgart, 1963, pages 61 to 70, and by W. Siefken, Liebigs Annalen der Chemie, Volume 562, pages 75 to 136. Suitable examples are the polyurethane prepolymers containing isocyanate groups that can be prepared by reacting polyols with an excess of polyisocyanates and are preferably of low viscosity.

Further examples of suitable polyisocyanates are polyisocyanates containing isocyanurate, biuret, allophanate, iminooxadiazinedione, urethane, urea and/or uretdione groups. Polyisocyanates containing urethane groups, for example, are prepared by reacting some of the isocyanate groups with polyols, such as trimethylolpropane and glycerol, for example. Preference is given to the use of aliphatic or cycloaliphatic polyisocyanates, especially hexamethylene diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, dicyclohexylmethane

2,4'-diisocyanate, dicyclohexylmethane 4,4'-di-
isocyanate, or 1,3-bis(isocyanatomethyl)cyclohexane,
diisocyanates derived from dimeric fatty acids, as sold
under the commercial designation DDI 1410 by Henkel,
5 1,8-diisocyanato-4-isocyanatomethyloctane, 1,7-diiso-
cyanato-4-isocyanatomethylheptane or 1-isocyanato-2-(3-
isocyanatopropyl)cyclohexane, or mixtures of these
polyisocyanates.

- 10 Very particular preference is given to using mixtures
of polyisocyanates containing uretdione and/or
isocyanurate and/or allophanate groups, based on
hexamethylene diisocyanate, as formed by catalytic
oligomerization of hexamethylene diisocyanate using
15 appropriate catalysts. The polyisocyanate constituent
may further comprise any desired mixtures of the free
polyisocyanates exemplified.

Examples of suitable blocking agents are the blocking
20 agents known from the U.S. patent US-A-4 444 954, such
as

i) phenols such as phenol, cresol, xlenol,
nitrophenol, chlorophenol, ethylphenol, t-butyl-
phenol, hydroxybenzoic acid, esters of this acid,
25 or 2,5-di-tert-butyl-4-hydroxytoluene;

ii) lactams, such as ϵ -caprolactam, δ -valerolactam,
 γ -butyrolactam or β -propiolactam;

iii) active methylenic compounds, such as diethyl malonate, dimethyl malonate, ethyl or methyl acetoacetate, or acetylacetone;

5 iv) alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, n-amyl alcohol, t-amyl alcohol, lauryl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, 10 diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, propylene glycol monomethyl ether, methoxymethanol, glycolic acid, glycolic esters, lactic acid, lactic esters, methylolurea, methylolmelamine, diacetone alcohol, ethylenechlorohydrin, ethylenebromohydrin, 1,3- 15 dichloro-2-propanol, 1,4-cyclohexyldimethanol or acetocyanohydrin;

20 v) mercaptans such as butyl mercaptan, hexyl mercaptan, t-butyl mercaptan, t-dodecyl mercaptan, 2-mercaptobenzothiazole, thiophenol, methylthiophenol or ethylthiophenol;

25 vi) acid amides such as acetoanilide, acetoanisidinamide, acrylamide, methacrylamide, acetamide, stearamide or benzamide;

vii) imides such as succinimide, phthalimide or maleimide;

5

x) ureas such as urea, thiourea, ethyleneurea, ethylenethiourea or 1,3-diphenylurea;

10

xii) imines such as ethyleneimine;

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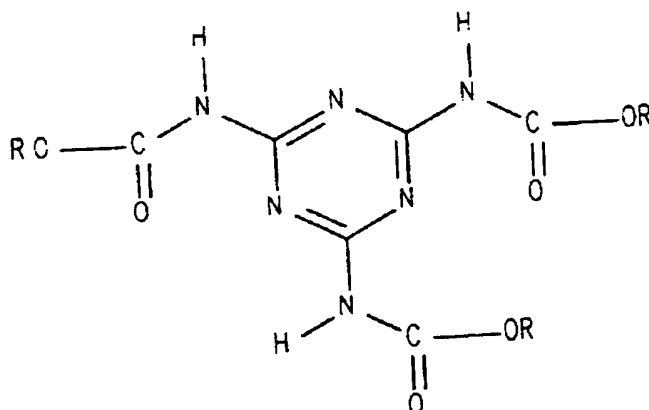
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xvi) substituted pyrazoles, ketoximes, imidazoles or triazoles; and also

mixtures of these blocking agents, especially dimethylpyrazole and triazoles, malonic esters and acetoacetic esters or dimethylpyrazole and succinimide.

- 5 As crosslinking agent (a7) it is also possible to use tris(alkoxycarbonylamino)triazines of the general formula 5



- 10 Examples of suitable tris(alkoxycarbonylamino)-triazines (a7) are described in the patents US-A-4 939 213, US-A-5 084 541, and EP-A-0 624 577. Use is made in particular of the tris(methoxy-, tris-
15 (butoxy- and/or tris(2-ethylhexoxycarbonylamino)triazines.

- The methyl butyl mixed esters, the butyl 2-ethylhexyl mixed esters, and the butyl esters are of advantage.
20 They have the advantage over the straight methyl ester of better solubility in polymer melts, and also have less of a tendency to crystallize out.

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In particular as crosslinking agents (a7) it is possible to use amino resins, examples being melamine resins. Any amino resin suitable for transparent topcoats or clearcoats, or a mixture of such amino resins, may be used. Especially suitable are the customary and known amino resins some of whose methylo and/or methoxymethyl groups have been defunctionalized by means of carbamate or allophanate groups. Crosslinking agents of this kind are described in the patents US-A-4 710 542 and EP-B-0 245 700 and also in the article by B. Singh and coworkers, "Carbamylmethylated Melamines, Novel Crosslinkers for the Coatings Industry" in Advanced Organic Coatings Science and Technology Series, 1991, Volume 13, pages 193 to 207. Moreover, the amino resins may also be used as binders (a1) in the base paint (A1).

Further examples of suitable crosslinking agents (a7) are beta-hydroxyalkylamides such as N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide or N,N,N',N'-tetrakis(2-hydroxypropyl)adipamide.

Further examples of suitable crosslinking agents (a7) are siloxanes, especially siloxanes containing at least one trialkoxy- or dialkoxysilane group.

Further examples of suitable crosslinking agents (a7) are polyanhydrides, especially polysuccinic anhydride.

If the coating material I includes a resin (a1) containing no functional groups (a12), the constituent (a7) is mandatorily present in the coating material I. In accordance with the invention, it is of advantage in this case if the above-described binders (a7) are used for this purpose.

All in all, it is of advantage for the coating material of the invention if the complementary functional groups (a12) and (a22), especially hydroxyl groups and the isocyanate groups, are present in a molar ratio OH/NCO of from 0.5 to 2:1, with particular preference from 0.8 to 1.5:1, with very particular preference from 0.8 to 1.2:1, and in particular from 0.8 to 1.0:1.

The coating material I for use in accordance with the invention may be present in different forms. For instance, given an appropriate choice of its above-described constituents, it may be present as a liquid coating material I which is essentially free from organic solvents and/or water. However, the coating material I may also comprise a solution or dispersion of the above-described constituents in water and/or organic solvents. Furthermore, the coating material I, given an appropriate choice of its above-described constituents, may be a powder clearcoat material I. This powder clearcoat material I may be dispersed if desired in water, so giving a powder slurry clearcoat material I. If the reactivity of its constituents (a1)

and/or (a7) on the one hand and (a2) on the other permits, the coating material I may be a one-component system. If, however, there is a risk of the abovementioned constituents undergoing premature thermal crosslinking, it is advisable to configure the coating material I as a two-component or multicomponent system, in which at least the constituent (a2) is stored separately from the remaining constituents and is not added to them until shortly before use.

10 In the second process step, a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally is applied to the partially cured clearcoat film I.

15 The coating material II may also be present as a liquid, solution, dispersion, powder clearcoat material or powder slurry clearcoat material I. It is applied using the methods described above for the coating material I. It is of advantage in accordance with the invention to apply the coating material II in a wet film thickness such that, after curing, the clearcoat II in the clearcoat system A of the invention has a dry film thickness of preferably from 2 to 15, with particular preference from 3 to 10, and in particular from 4 to 8 μm .

The substantial constituents of the coating material II are nanoparticles, especially those based on silicon

dioxide, aluminum oxide and zirconium oxide. They have a particle size of less than 50 nm, and have no flattening effect. Preferably, nanoparticles based on aluminum oxide and zirconium oxide are used.

5

Examples of suitable nanoparticles based on silicon dioxide are pyrogenic silicas, which are sold under the trade name Aerosil® VP8200, VP721 or R972 by Degussa or under the trade names Cab O Sil® TS 610, CT 1110F or CT 1110G by Cabot.

In general, these nanoparticles are sold in the form of dispersions in monomers curable with actinic radiation, such as the reactive diluents (a5) described above.

such as the reactive diols.

15 Examples of suitable monomers which are especially suitable for the present application are alkoxyated pentaerythritol tetraacrylate or triacrylate, ditrimethylolpropane tetraacrylate or triacrylate, dineopentyl glycol diacrylate, trimethylolpropane

20 triacrylate, trishydroxyethyl isocyanurate triacrylate, dipentaerythritol pentaacrylate or hexaacrylate, or hexanediol diacrylate. In general, these dispersions contain the nanoparticles in an amount, based in each case on the dispersions, of from 10 to 80% by weight,

25 preferably from 15 to 70% by weight, with particular preference from 20 to 60% by weight, and in particular from 25 to 50% by weight.

An example of a nanoparticle dispersion which is especially suitable in accordance with the invention is the dispersion sold under the trade name High Link® OG 103-31 by Clariant Hoechst.

5

The nanoparticle dispersions are present in the coating material II advantageously in an amount of from 2 to 30% by weight, with particular preference from 3 to 25% by weight, and in particular from 5 to 20% by weight, based in each case on the overall amount of the coating material II.

10
15
20
The coating material II further comprises a resin curable with actinic radiation. Examples of suitable resins curable with actinic radiation come from the oligomer and polymer classes which are described above in connection with the resin (a1). It is of advantage in accordance with the invention if the resins used in the coating material II have no functional groups (a12) or (a22). Of these resins, the urethane (meth)acrylates and the (meth)acrylate oligomers have particular advantages and are therefore used with particular preference in accordance with the invention.

25
The resin is employed advantageously in an amount of from 5 to 90% by weight, with particular preference from 10 to 80% by weight, and in particular from 20 to 70% by weight, based in each case on the overall amount of the coating material II.

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Furthermore, the coating material II may include the constituents (a3), (a4), (a5), (a6) and/or (a7) described above in connection with the coating material I, in the amounts specified there.

5

In a procedure in accordance with the invention, the clearcoat films I and II are cured conjointly with actinic radiation and thermally in the process step 3. Here too, the apparatus and methods described above in connection with the partial curing of the clearcoat film I are employed.

10 In the alternative process A of the invention, which has particular advantages for automotive refinish in particular, the applied clearcoat film(s) I are cured not partially but completely in the first process step, using the apparatus and methods described above. Subsequently, the outer surface of the clearcoat film(s) I is roughened. The customary and known roughening methods, such as rubbing with sandpaper or steel wool, or filing or brushing, are appropriate in this case. Thereafter, in the second process step, the above-described clearcoat film II is applied and is cured with actinic radiation and also, if desired, thermally, again using the apparatus and methods described above.

The clearcoats A of the invention described above, which are preferably produced with the aid of the

processes A of the invention, may also be part of the multicoat systems B of the invention. Advantageously, these systems are produced with the aid of the processes B of the invention.

5

For this purpose, the clearcoat film(s) I in the first process step is or are applied not to the primed or unprimed substrates but rather to at least one color and/or effect basecoat film III which is present thereon, comprising a pigmented coating material III curable thermally and also, if desired, with actinic radiation.

In accordance with the invention it is of advantage to apply the clearcoat film(s) I by the wet-on-wet technique to the dried or flashed off, but not cured, basecoat film III.

Thereafter, in a first variant of the process B of the invention, the basecoat film(s) III and the clearcoat film(s) I are partly cured. Subsequently, in the third process step, the clearcoat film II is applied, after which the basecoat film(s) III, clearcoat film(s) I and clearcoat film II are cured conjointly with actinic radiation and thermally.

In the second variant of the process B of the invention, in the third process step the basecoat film(s) III and the clearcoat film(s) I are fully

cured, after which in the fourth process step the outer surface of the clearcoat film(s) I is roughened. Thereafter, in the fifth process step, the clearcoat film II is applied and in the sixth process step it is
5 fully cured.

Suitable coating material III for the production of the basecoat film III comprises the customary and known basecoat materials, especially waterborne basecoat
10 materials.

Examples of suitable waterborne basecoat materials are known from the patents EP-A-0 089 497, EP-A-0 256 540, EP-A-0 260 447, EP-A-0 297 576, WO 96/12 747, EP-A-0 523 610, EP-A-0 228 003, EP-A-0 397 806, EP-A-0 574 417, EP-A-0 531 510, EP-A-0 581 211, EP-A-0 708 788, EP-A-0 593 454, DE-A-43 28 092, EP-A-0 299 148, EP-A-0 394 737, EP-A-0 590 484, EP-A-0 234 362, EP-A-0 234 361, EP-A-0 543 817, EP-A-0 522 420, WO 95/14 721, EP-A-0 521 928, EP-A-0 536 712, EP-A-0 522 419, EP-A-0 649 865, EP-A-0 584 818, EP-A-0 596 460, EP-A-0 596 461, EP-A-0 678 536, EP-A-0 669 356, EP-A-0 634 431, WO 97/49 745, EP-A-0 354 261, EP-A-0 424 705, EP-A-0 401 565, EP-B-0 730 613, and
20 WO 97/49 747, EP-A-0 401 565, EP-B-0 730 613, and
25 WO 95/14 721.

In the case of the processes B of the invention it is possible - as already mentioned - to employ all

application, curing and roughening methods and apparatus described above in connection with the coating material I.

5 Owing to their glasslike surface, the clearcoats A of the invention and the multicoat systems B of the invention have an extremely high scratch resistance. This advantageous property is supplemented by an outstanding optical properties profile and also
10 outstanding weathering stability and chemical resistance. As a result, motor vehicles, plastics parts, furniture and other parts for private or industrial use, including coils and containers, which comprise at least one clearcoat A of the invention
15 and/or at least one multicoat system B of the invention, are superior in their value, their service properties and their service life to products which comprise only conventional coatings.

20 **Examples 1 and 2 and comparative experiment C1**

The production of inventive clearcoat systems A (examples 1 and 2) and also a noninventive clearcoat system (comparative experiment C1)

25

In the case of examples 1 and 2 and in the case of the comparative experiment C1, a clearcoat film I of a coating material I was applied to PMMA test panels, was predried for 6 minutes and was partially cured using UV

radiation with an energy of 1 or 2 millijoules/cm². In all cases, the clearcoat film I was applied in a wet film thickness such that in the fully cured clearcoats of examples 1 and 2 and of the comparative experiment
5 C1 the resulting dry film thickness was from 25 to 27 µm.

The coating material I consisted of 100 parts by weight of a urethane (meth)acrylate which was free from
10 hydroxyl groups (Ebecryl® 5129 from UCB), 100 parts by weight of a polyesterpolyol (Desmophen® from Bayer AG), 2.5 parts by weight of a commercial photoinitiator (Irgacure® 819 from Ciba and Lucirin® TPO from BASF AG), 0.6 part by weight of a commercial UV absorber and
15 light stabilizer (mixture of Tinuvin® 400 and neutral HALS from Ciba and also a sterically hindered phenol) and 50 parts by weight of a commercial oligomeric acrylate containing free isocyanate groups and acrylate groups (Roskydal® 2545 from Bayer AG). For application,
20 the coating material I was adjusted to spray viscosity using a suitable organic solvent (mixture of butyl acetate, n-butanol and Ektapro®).

The coating material II was applied over the partially
25 cured clearcoat film I, in a wet clearcoat film thickness II such that complete curing resulted in a dry film thickness of from 4 to 6 µm.

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In the case of example 1, the coating material II consisted of 30 parts by weight of a commercial (meth)acrylate oligomer (Ebecryl® IRR351 from UCB), 10 parts by weight of a commercial reactive diluent (Servocure® RTT 192 from Servo Delden), 10 parts by weight of a commercial dispersion of nanoparticles in a polyfunctional monomer (High Link® OG 103-31 from Clariant Hoechst), 2 parts by weight of a commercial photoinitiator (Lucirin® TPO from BASF AG), 1 part by weight of a commercial UV absorber (Cyagard 1164L from Cytec), and 0.05 part by weight of a commercially customary, siloxane-based wetting agent. For application, the coating material I was adjusted to spray viscosity (solids content about 30 to 40% by weight) using an appropriate organic solvent (mixture of butyl acetate, n-butanol and Ektapro®).

The coating material II of example 2 corresponded to that of example 1 except that in this case an additional 10 parts by weight of silica (Aerosil®) were present.

The coating material II of the comparative experiment C1 corresponded to the coating material of example 1 except that in this case no High Link® OG 103-31 was present.

In examples 1 and 2 and in the comparative experiment C1, the clearcoat films I and II were fully cured,

following a rest period of 6 minutes at from 50 to 60°C, with UV radiation (from 1 to 3 joules/cm²) and thermally (10 minutes at 90°C).

- 5 The clearcoats were subjected to the Taber 5131 abrasion test with 100 and 500 cycles with a load of one kilogram per arm. Appropriate equipment is available from ERICHSEN, F-92508 Rueil-Malmaison, Cedex, France. After the test, the haze was determined
- 10 in accordance with DIN 67530. For comparison, the abrasion resistance of uncoated PMMA and PC plastic panels was measured. The table gives an overview of the results obtained. The comparison of the haze values in the table demonstrates the superior scratch resistance
- 15 of the clearcoats A of the invention, which are outstandingly suitable for imparting scratch resistance to sensitive surfaces of plastic.

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Table: The haze values (losses in light transmissivity, in percent) of the inventive (examples 1 and 2) and the noninventive (comparative experiment C1) clearcoats

5

Example or comparative experiment no.	Loss of light transmissivity after:	
	100 cycles (%)	500 cycles (%)
C1	8	22
1	4	11
2	3	9
PMMA (for comparison)	30	41
PC (for comparison)	46	59

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10 Additionally, the inventive clearcoats of examples 1 and 2 were subjected to the key test, which is relevant for everyday practice. For this purpose, they were scored under load with a BIC® pen having a ball of 2 mm in diameter. Here it was found that the inventive clearcoats were scratchable only at loads above 2 000 g. The corresponding load in the case of the siloxane-containing baking clearcoat, used as standard

15 in this test, is 500 g.